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Infrared Spectroscopy of Molecular Ions  
of Astrophysical Interest

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The object of my research for the NASA grant NAGW-4769 was to observe infrared spectra of molecular ions with special astrophysical interest in plasmas both in the laboratory and in space. Progress made during the period from September 1995 to September 1996 is summarized in the following.

1. Detection of Interstellar  $H_3^+$

The discovery of interstellar  $H_3^+$  through its mid-infrared absorption spectrum was by far the most inspiring development during this fiscal year.  $H_3^+$ , the simplest stable polyatomic system, has been postulated to play the central role in the ion-neutral reaction scheme of interstellar chemistry, but its presence had not been directly observed in spite of intensive searches by several groups. Ever since the observation of the  $H_3^+$   $\nu_2$ -fundamental band in 1980, I had been searching for it in interstellar space in collaboration with T. R. Geballe of the United Kingdom Infrared Telescope (UKIRT). Recent phenomenal improvement in the sensitivity of the observational infrared spectrometer has finally led us to its successful detection.

The infrared spectrum of  $H_3^+$  at  $3.7\text{ }\mu\text{m}$  was observed on three nights of April 29, June 10, and July 15 in 1996.<sup>1</sup> The observations were made using the CGS4 Spectrometer with a resolving power of  $\sim 15,000$  at UKIRT on Mauna Kea, Hawaii. We have noted clear doublet

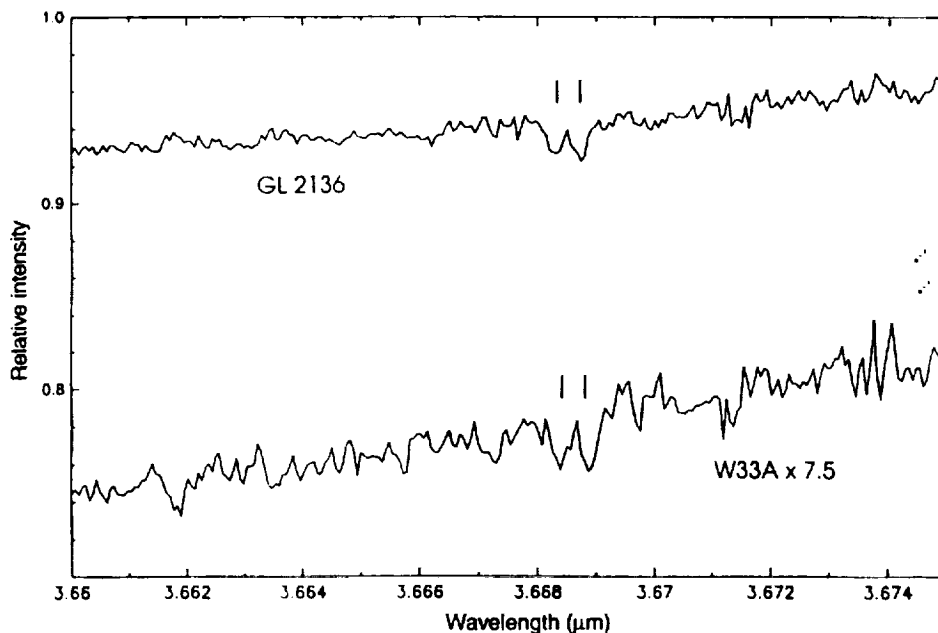


Fig. 1. The  $H_3^+$  doublet  $R(1,0)$  at  $3.66852\text{ }\mu\text{m}$  and  $R(1,1)^+$  at  $3.66808\text{ }\mu\text{m}$  in dense molecular clouds toward YSO GL2136 and W33A.<sup>1</sup>

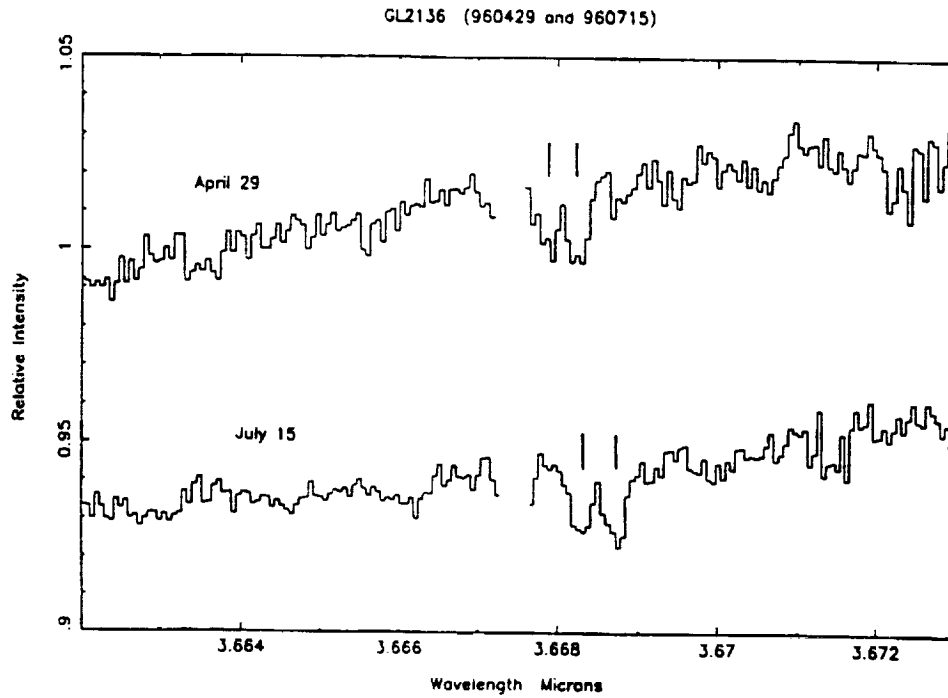


Fig. 2. Spectral lines of GL2136 obtained in 1996 April and July. The wavelengths of the lines are shifted by Doppler effect due to the earth's orbital motion.

composed of the  $R(1,0)$  transition of ortho- $H_3^+$  and the  $R(1,1)^+$  transition of para- $H_3^+$  in dense clouds towards the deeply embedded young stellar objects (YSO) GL2136 and W33A (Fig. 1). We were convinced of the authenticity of the weak signals because of their Doppler shifts over the three months from April to July due to the earth's motion (Fig. 2).

The equivalent widths of the observed spectrum demonstrated the  $H_3^+$  column densities of  $4.0 \times 10^{14} \text{ cm}^{-2}$  and  $6.0 \times 10^{14} \text{ cm}^{-2}$  for GL2136 and W33A, respectively. The observation provides the most direct evidence supporting the ion-neutral reaction scheme of interstellar chemistry initially proposed by Herbst and Klemperer, and by Watson in 1973. The observation has introduced the infrared spectrum of  $H_3^+$  as a powerful probe to monitor interstellar hydrogenic molecular species and led to subsequent exciting observations.

## 2. Observation of High Rovibrational States of $H_3^+$

The initial discovery of  $H_3^+$  in the Jovian auroral region was made through the identification of the  $2\nu_2^2 \rightarrow 0$  overtone band indicating the population of  $H_3^+$  in high rovibrational state. While the Einstein coefficient for spontaneous emission is higher for the overtone band than for the hot band  $2\nu_2^2 \rightarrow \nu_2^2$  because of the  $\nu^3$  factor, the spectral lines corresponding to the latter still have sufficient intensities to be observed with reasonable signal to

noise ratios. Since such spectrum appear in the same wavelength region as that for the fundamental band, we can determine temperature accurately by comparing intensities of spectral lines belonging to the two bands.

We have observed ten spectral lines in the South Pole auroral region of Jupiter encompassing all three infrared active hot bands  $2\nu_2^2 \rightarrow \nu_2^1$ ,  $2\nu_2^0 \rightarrow \nu_2^1$ , and  $\nu_1 + \nu_2 \rightarrow \nu_1$ . A spectrum in the  $3.84 \mu\text{m}$  region which is particularly rich in the  $2\nu_2^2 \rightarrow 2\nu_2^1$  hot band lines is shown in Fig. 3.

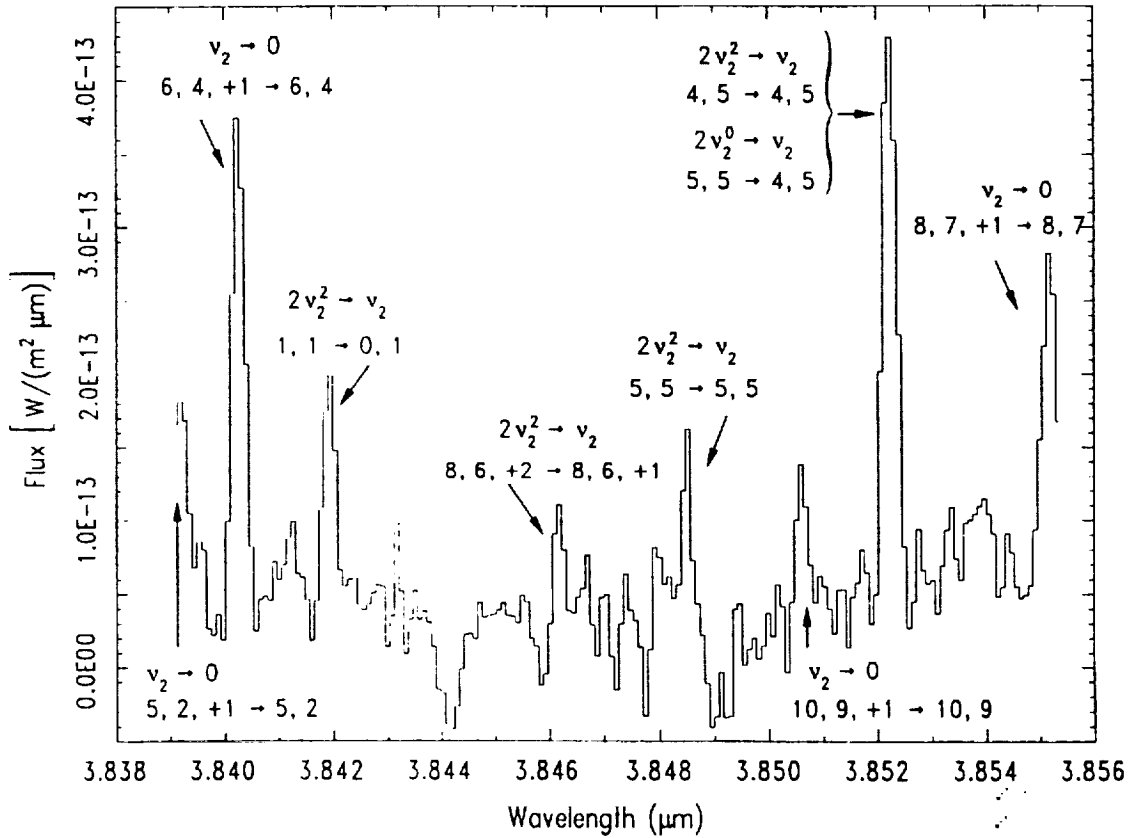


Fig. 3.  $\text{H}_3^+$  hot band emission lines together with weaker fundamental band emission lines observed in the South Pole of Jupiter. The CCS4 spectrometer of UKIRT was used.

The relative intensities of the spectral lines belonging to the hot band and the fundamental band, together with accurate theoretical line strengths, leads us to an accurate temperature of the region. Since we also observe different vibrational modes  $2\nu_2^2$ ,  $2\nu_2^0$ , and  $\nu_1 + \nu_2^1$ , it is potentially possible to sense the dependence of relaxation on vibrational modes.<sup>3</sup>

Our laboratory attempt to observe pure rotational spectrum of  $\text{H}_3^+$  induced by the breakdown of geometry due to centrifugal distortion<sup>4</sup> has not been successful due to the weakness of the transitions. Observation of such spectrum in space in the excited state and in the ground state was discussed with K. Kawaguchi of the Nobeyama Radio Observatory and A. Betz at the University of Colorado. The intensity of the former was estimated to be not sufficient; the latter has to wait the start of the SOPHIA project.

### 3. Observation of Ortho-Para $\text{H}_3^+$ Selection Rules in Plasma Chemistry<sup>5-7</sup>

Selection rules that relate quantum states before and after various processes are fascinating subjects based on the symmetry argument. It is well known that the ordinary radiative processes, i.e., spectroscopy, obey most rigorous selection rules while molecular collisional processes obey less rigorous rules.<sup>8</sup> In both processes, however, selection rules related to nuclear spin quantum numbers hold most rigorously because of the weakness of nuclear magnetic interactions. We have demonstrated experimentally that such selection rules hold even for the most violent of molecular processes, that is, chemical reactions. Our experimental results address most directly the classic theoretical prediction by Quack<sup>9</sup> in that (a) we study a network of ion-neutral reactions in plasmas in which many protons are scrambled and (b) we study spin modifications of polyatomic molecules. The result of our experiment is intimately related to our interpretation of the relative abundance of ortho- and para- $\text{H}_3^+$  in interstellar space.

The principle of our experiment is quite simple. We observe relative intensities of closely spaced infrared spectral lines of ortho- $\text{H}_3^+$  ( $I = 3/2$ ) and para- $\text{H}_3^+$  ( $I = 1/2$ ) using normal- $\text{H}_2$  and para- $\text{H}_2$  as discharge gases. If the spin memory survives the chemical reaction, we should see dependence of the relative intensity on the spin modifications of the discharge gases. We have conducted experiments using a hollow cathode discharge cell with both continuous AC discharge and pulsed discharge, and a positive column discharge cell with a continuous AC discharge. All experiments showed that the para- $\text{H}_3^+$  to ortho- $\text{H}_3^+$  ratio increased significantly when para- $\text{H}_2$  was used instead of normal  $\text{H}_2$ , clearly demonstrating the existence of nuclear spin selection rules in plasma chemistry.

A result of a hollow cathode pulsed discharge experiment is shown in Fig. 4. It is noted that the para- $\text{H}_3^+$  to ortho- $\text{H}_3^+$  intensity ratio increases drastically from  $\sim 0.35$  for the o- $\text{H}_2$

discharge to  $\sim 2.3$  for  $p\text{-H}_2$  discharge (30  $\mu\text{s}$  after the beginning of the pulse) demonstrating the selection rules. A detailed analysis of the results has explained the discharge gas dependence of the ortho-para ratio and its temporal variations quantitatively. In the analysis, we extended Quack's theory for counting branching ratios of different spin modifications.

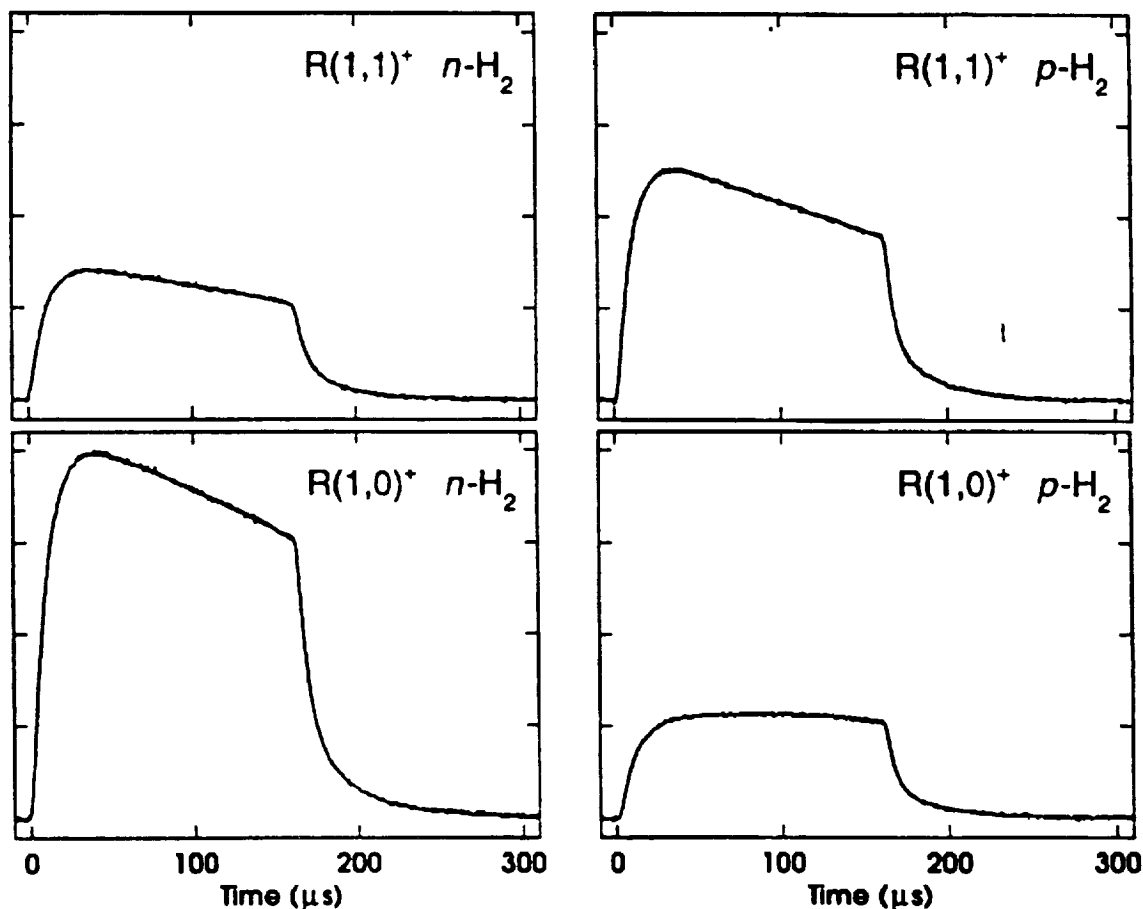


Fig. 4. Observed time variation of the peak intensities of the  $R(1,1)^+$  para- $\text{H}_3^+$  infrared absorption (upper trace) and the  $R(1,0)^+$  ortho- $\text{H}_3^+$  absorption (lower trace). The absorption intensities are in an arbitrary scale which is common to all four traces.

#### 4. Spectroscopy of Other Ions

**Carbocations.** Spectroscopy of carbocations  $\text{CH}_3^+$ ,  $\text{CH}_2^+$ ,  $\text{C}_2\text{H}_3^+$  and  $\text{C}_2\text{H}_2^+$  has been continued. The identification of the main rovibrational structure of their antisymmetric C-H stretch band had been already made, but we needed to identify their weaker spectral lines such as those from high rotational levels, hot bands, symmetric C-H stretch band, combination and overtone bands, etc. This is for paving the way to the next project, i.e., the spectroscopy of  $\text{CH}_5^+$ . The weak

spectral lines for the C–H stretch band of  $\text{CH}_5^+$  appear amidst the bush of many carbocation spectral lines, and it is necessary to “weed out” those lines. The most confusing ones are those of  $\text{CH}_3^+$  hot bands starting from the  $\nu_2/\nu_4$  bending excited states. We attempted to first decipher the spectrum of the  $\nu_2/\nu_4$  fundamental bands using our diode spectrum, but this has not been successful because of the extraordinarily strong Coriolis coupling between these states. We then resorted to chemical method, that is, discriminating spectral lines of different carbocations by their plasma chemical behavior. This was completed and  $\text{CH}_5^+$  spectral lines were finally identified with confidence.

**$\text{NH}_2^+$ .** The amidogen ion,  $\text{NH}_2^+$ , was studied using high temperature He-dominated plasmas from 2900–3500  $\text{cm}^{-1}$  and four hot bands  $2\nu_2^0 + \nu_3 \leftarrow 2\nu_2^0$ ,  $\nu_1 + \nu_3 \leftarrow \nu_1$ ,  $\nu_1 + \nu_2 + \nu_3 \leftarrow \nu_1 + \nu_2$ , and  $2\nu_1 + \nu_3 \leftarrow 2\nu_1$  have been observed and characterized.<sup>10</sup> This is an extremely quasilinear molecule with the barrier to linearity of only 155  $\text{cm}^{-1}$  in its  $\tilde{X}^3\text{B}_1$  electronic ground state and its behavior in the excited bending  $\nu_2$  state is of special interest for theorists.<sup>11</sup>

**$\text{HeH}^+$  and Isotopomers.** With the support of a JSPS fellowship for research in Japan, I spent one month in the Department of Physics, Toyama University in the summer of 1996 to set up a far infrared molecular ion spectrometer. Because of the hard work and excellence of Professors Takagi and Matsushima, and their students, the collaboration was extremely successful, and we observed low J rotational transitions of  $\text{HeH}$  and its D and  $^3\text{He}$  isotopomers.<sup>12</sup> The results provide crucial data for the breakdown of the Born-Oppenheimer approximation for this most fundamental species. The  $J = 1 \rightarrow 0$  transition of  $\text{HeH}^+$  will be the most powerful probe for a search of this important ion in astronomical objects.<sup>13</sup>

**Others.** Other papers on this project published after submitting my proposal on June 30, 1994 are listed.<sup>14–19</sup>

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